5. A 31.7% yield of 2-phenylbenzothiazole results from the reaction between phenyllithium and benzothiazole.

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[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Reactions of Vanillin and its Derived Compounds. VIII.[1] The Ultraviolet Absorption of Vanillic Acid and Related Acids and their Esters[2,3]

BY IRWIN A. PEARL

A large number of esters of vanillic acid and related acids have been prepared recently and their toxicities toward representative microörganisms have been reported.[1,4] In addition, their use as food preservatives has been described.[5] Preliminary observations which indicated that certain compounds in this series possessed marked absorption in the ultraviolet region of the spectrum led to a comprehensive study of the ultraviolet absorption characteristics of vanillic acid, its esters, and its related compounds, and of possible uses for these materials.

The esters of vanillic, orthovanillic and 5-chlorovanillic acids previously described were employed as samples in this study. The ultraviolet absorption spectra of these compounds were determined in specially purified dioxane solution with the model DU Beckman quartz spectrophotometer employing 1.0-cm. quartz cells. Each reading was made at minimum slit width and, therefore, at minimum sensitivity. The narrow slit width was used, with the corresponding sacrifice in sensitivity, in order to obtain more accurately the exact shape of the absorption curve.

Vanillic Acid.—The ultraviolet absorption spectrum of vanillic acid is given in Curve 2 of Fig. 1. Three primary absorption bands are indicated. These have their maxima at 2900, 2590 and approximately 2200 Å., respectively. In addition, secondary maxima appear at 2630, 2530 and 2470 Å. The three primary absorption bands were expected on the basis of recorded data, but the positions of these bands are not in accord with that expected from a knowledge of the literature.

In a comprehensive study of the ultraviolet absorption characteristics of pure compounds related to lignin, Patterson and Hibbert[6] found that compounds possessing the guaiacyl structure exhibited three absorption bands in the ultraviolet, characterized by maxima at 3060, 2800 and 2305 Å., these being due, respectively, to the presence of a side chain chromophore in conjugation with the ring, to freedom of the position meta to the point of attachment of the side chain, and to some unexplained characteristic of the aromatic nucleus. These authors examined vanillin, eugenol, isoeugenol, coniferin, and many derivatives of propylguaiacol, but did not examine any derivatives of vanillic acid. The spectrum of α-hydroxypropiovanillone obtained by Aulin-Erdtman[7] concurs with spectra obtained by Patterson and Hibbert. All these spectra were obtained in ethanol.

We have obtained the ultraviolet absorption spectrum of vanillin in purified dioxane. This curve (Curve 1 of Fig. 1) has maxima at 3090, 2740 and 2275 Å. and, when compared with curves in the literature for vanillin in other solvents (see Table I), clearly indicates the effect of solvent on the ultraviolet absorption spectrum, and the variation in spectra determined by different experimenters employing the same solvent.

It is evident from a comparison of Curves 1 and 2 of Fig. 1 that the presence of a –CO–O– group attached to a ring para to the hydroxyl group has caused hypsochromic shifts of the principal maxima. In addition three secondary maxima have appeared. These secondary maxima have never been recorded in previous studies of guaiacyl derivatives.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF VANILLIN IN VARIOUS SOLVENTS

Solvent	Maxima, Å.		
Hexane[a]	3000	2670	2230
Ethanol[a]	3080	2810	2290
Ethanol[b]	3120	2780	
Ethanol[c]	3080	2780	2320
Water[a]	3310	2910	
Dioxane[d]	3040	2740	2275

[a] Herzog and Hillmer, *Ber.*, **64B**, 1288 (1932). [b] Russell, Todd and Wilson, *J. Chem. Soc.*, 1940 (1934). [c] Ref. 6. [d] Present paper.

Ultraviolet absorption curves were obtained for a large number of esters of vanillic acid. These curves (see Table II) for the most part are almost identical with that of vanillic acid, except for actual specific extinction values. In several instances, some of the secondary maxima have been reduced to breaks in the curve. In others, the presence of new groupings in the non-vanillic acid portion of the molecule has resulted in shifts of the principal maxima, as well as changes in the secondary maxima.

The spectrum for ethyl vanillate is illustrative of a case in which the 2470 Å. maximum has been reduced to a break in the curve. The spectrum for phenyl vanillate represents a case in which a principal maximum is shifted to a higher wavelength and three secondary maxima have been reduced to breaks in the curve.

The presence of halogen in the ester grouping exerts a different effect, depending upon the type of ester group and the position of the halogen in the group. 2-Chloroethyl vanillate has a break in the curve at 2650 Å. The principal maximum is at 2630 Å. as in vanillic acid, ethyl vanillate, etc. In the spectra of all the other halogenated derivatives, a bathochromic shift takes place and this maximum occurs at a slightly higher wave length. The

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[1] For paper VII of this series, see THIS JOURNAL, **71**, 1066 (1949).

[2] Presented before the Division of Organic Chemistry at the 113th meeting of The American Chemical Society, Chicago, Illinois, April 19–23, 1948.

[3] This paper represents a portion of the results obtained in the research program sponsored by The Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

[4] Pearl and McCoy, THIS JOURNAL, **69**, 3071 (1947).

[5] Pearl and McCoy, *Food Industries*, **17**, 1458 (1945).

[6] Patterson and Hibbert, THIS JOURNAL, **65**, 1862 (1943).

[7] Aulin-Erdtman, *Svensk Papperstidn.*, **47**, 91 (1944).

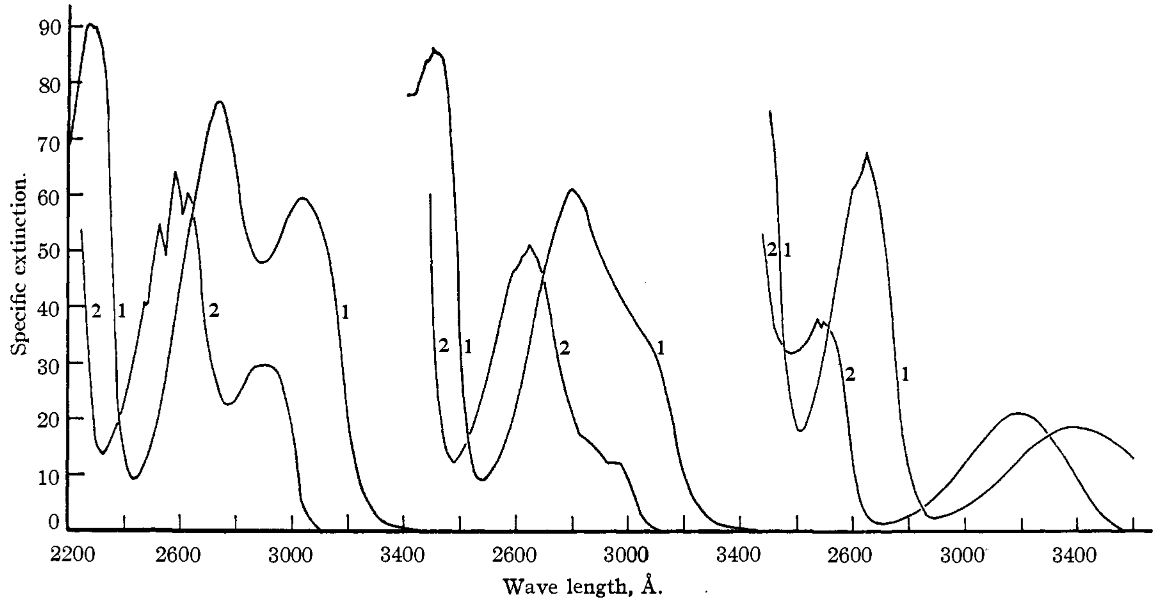

Fig. 1.—Curve 1, vanillin; curve 2, vanillic acid.
Fig. 2.—Curve 1, 5-chlorovanillin; curve 2, 5-chlorovanillic acid.
Fig. 3.—Curve 1, orthovanillin; curve 2, orthovanillic acid.

presence of more than one chlorine causes the bathochromic shift of the 2775 Å. minimum to 2800 Å. or higher. The presence of an ether linkage in the ester group, as in the cases of the Cellosolve (alkoxyethyl) and Carbitol (alkoxyethoxyethyl) esters, has little effect upon the location of the maxima and minima. The presence of a phenyl group in the ester group, whether attached to the vanillic acid directly through an ester linkage or otherwise, causes bathochromic shifts of some bands to higher wave lengths.

5-Chlorovanillic Acid.—The effect of substitution on the absorption spectra of vanillic acid esters was then studied. The spectrum for 5-chlorovanillic acid is shown in Fig. 2,

TABLE II

ABSORPTION SPECTRA OF ESTERS OF VANILLIC ACID

Ester	Max. 2900[a]	Min.		Max.		Min. 2610[b]	Max. 2590[c]	Min. 2550[d]	Max. 2530[e]	Min.		Breaks in curve,
	k[f]	λ	k	λ	k	k	k	k	k	λ	k	λ
Et	26.9	2775	20.2	2630	54.6	52.1	56.7	46.3	49.4	2325	11.7	2470
Et_2CHCH_2	22.4	2775	16.8	2630	44.3	40.1	45.4	34.4	38.5	2325	9.5	2470
CH_2ClCH_2	25.0	2780	19.7	2630	42.1	36.6	39.4	33.6	34.4	2350	9.1	2650
$MeCHClCH_2$	24.1	2780	18.6	2650	46.9	40.8	45.5	32.9	35.6	2350	8.4	2470
$CH_2ClCH_2CH_2$[g]	23.4	2775	18.1	2650	44.5	36.9	42.2	29.5	32.8	2325	9.7	2420
$(CH_2Cl)_2CH$	21.7	2800	16.9	2650	40.7	35.6	36.9	26.1	26.4	[h]		2470
$CH_2ClCHClCH_2$	21.8	2810	16.9	2650	41.1	36.3	37.8	26.8	27.1	[h]		2470
CCl_3CMe_2	18.6	2810	15.0	2675	36.3	25.7	26.2			[h]		
CH_2OHCH_2	30.4	2800	24.4	2640	56.9	56.1	58.0			[h]		2530
$MeCHOHCH_2$	24.4	2775	18.0	2640	46.3	41.0	45.3	33.7	36.2	[h]		2470
$MeOCH_2CH_2$[i]	25.0	2775	18.8	2640	48.8	43.1	49.3	36.2	39.7	2325	10.0	
$BuOCH_2CH_2$	21.1	2775	16.0	2640	41.9	38.3	42.7	32.1	34.9	2325	8.6	2470
$Et_2CHCH_2OCH_2CH_2$[j]	19.5	2775	14.9	2640	37.3	32.0	36.9	26.8	29.2	2325	8.5	2420
$PhOCH_2CH_2$	20.3	2825	17.6	2640	43.8	38.5	42.1	31.3	33.1	2350	9.2	2750, 2470
$MeOCH_2CH_2OCH_2CH_2$[k]	21.8	2775	16.6	2640	41.5	35.3	39.9	28.4	31.0	2325	9.2	2420
$EtOCH_2CH_2OCH_2CH_2$	26.1	2800	20.0	2640	48.9	43.0	48.0	35.2	28.2	2350	10.4	2470
C_2H_4-bis	31.3	2775	24.3	2630	60.1	57.2	58.7			[h]		2530
*p*H	32.5	2825	27.2	2650	61.1					2375	15.4	2590, 2530, 2460
o-C_6H_4	29.4	2850	27.4	2650	53.8	46.5	47.0			2350	11.5	2530, 2470

[a] Maxima at 2900 A. except for no. 6 (2920 Å.) and 18 (2925 Å.). [b] Minima at 2610 Å. except for no. 19 (2600 Å.). [c] Maxima at 2590 Å. except for no 17 (2600 Å.). [d] Minima at 2550 Å. except for no. 6 and 7 (2540 Å.). [e] Maxima at 2530 Å. except for no. 3 (2540 Å.). [f] k represents specific extinction. [g] Additional minimum at 2480 Å. (k = 23.7) and maximum at 2470 Å. (k = 24.4). [h] This minimum not recorded because spectral data were not obtained at sufficiently low wave lengths. [i] Additional minimum at 2480 Å. (k = 28.3) and maximum at 2470 Å. (k = 28.6). [j] Additional minimum at 2480 Å. (k = 21.1) and maximum at 2470 Å (k = 21.8). [k] Additional minimum at 2480 Å. (k = 22.4) and maximum at 2470 Å. (k = 2 .0).

TABLE III

ABSORPTION SPECTRA OF ESTERS OF ORTHOVANILLIC ACID

	Max.		Min.		Max.		Min.		Max.		Min.	
	λ	*k*	λ	*k*	λ	*k*	λ	*k*	λ	*k*	λ	*k*
Me	3200	21.5	2700	1.4	2500	37.6	2490	36.9	2475	38.3	2375	31.8
Et	3200	16.9	2800	4.8	2515	30.8	2495	29.7	2475	31.2	2400	25.8
Pr	3200	18.5	2700	1.2	2510	32.8	2500	32.1	2475	33.6	2390	28.1
Iso-Bu	3200	17.3	2700	1.2	2500	31.4	2490	31.3	2475	31.5	2375	26.4
Bu	3200	17.2	2700	0.7	2510	30.9	2490	30.0	2475	32.6	2375	24.4
Iso-Am	3200	15.8	2700	0.9	2515	29.4	2495	28.6	2470	29.9	2375	22.9
Am	3200	16.5	2700	1.0	2515	29.3	2495	28.7	2470	29.6	2375	24.3
Et_2CHCH_2	3200	15.2	2700	0.6	2515	27.4	2495	26.8	2475	27.7	2375	21.7
$EtOCH_2CH_2$	3200	16.4	2700	1.1	2520	29.1	2495	28.6	2475	29.6	2375	24.0
$PhOCH_2CH_2$[a]	3200	13.2	2850	2.2	2520	26.2	2485	25.2	2475	25.5	2375	18.0
Ph[b]	3250	16.3	2850	3.6					2530	43.8	2390	30.4

[a] Additional maxima at 2775, 2710, and minima at 2750, 2675 Å. [b] Break in curve at 2570 Å.

Curve 2. The most striking effect of chlorination of vanillic acid in the 5-position is the removal of the principal absorption band having a maximum at 2900 Å., leaving only a break in the curve, and the bathochromic shift of the principal 2600 Å. maximum and 2320 Å. minimum to longer wave lengths. All other maxima have been reduced to breaks in the curve.

This curve is at variance with the conclusions of Patterson and Hibbert[8] concerning the cause of the 2800 Å. absorption band in guaiacyl derivatives. These authors state that the 2800 Å. absorption band (the middle band) of guaiacyl compounds is due to freedom of the position meta to the point of attachment of the side chain. Therefore, if this position is substituted, the 2800 Å. band should disappear. It has been shown above that, on going from vanillin to vanillic acid, the 2800 Å. maximum (actually, in dioxane this maximum is at 2740 Å.) is shifted to approximately 2600 Å., and the 3080 Å. maximum is shifted to 3040 Å. It is easily seen from Fig. 2 that substitution with chlorine in the free meta position has caused the disappearance of the original 3040 Å. band and not the 2600 Å. band. This should correspond to the 3080 Å. band in other guaiacyl compounds.

To further prove this point, the ultraviolet absorption spectrum of 5-chlorovanillin was compared with that of unsubstituted vanillin. The curve for 5-chlorovanillin is given in Fig. 2 (Curve 1). Again, it is the absorption band having the highest wave length (3050 Å.) and not the 2800 Å. band which has been reduced to a break in the curve. Chlorination of vanillin in the 5-position also affects the 2300 Å. band to some extent. Several new breaks appear in the curve.

Orthovanillic Acid.—The last variable studied was isomerization. Absorption spectra of esters of orthovanillic acid were obtained. These curves, represented by that for orthovanillic acid (Fig. 3), are characterized by two principal absorption bands having maxima at 3200 Å. and approximately 2500 Å. In addition, another absorption maximum at approximately 2200 Å. is indicated. The 2500 Å. maximum is composed of two separate maxima at about 2500 and 2475 Å. The maxima and minima of the absorption spectra of a number of esters of orthovanillic acid are tabulated in Table III. Very little difference exists between the various purely aliphatic esters. However, the presence of a benzene ring in the ester grouping causes marked changes in the curve. 2-Phenoxyethyl orthovanillate has two new maxima at 2775 and 2710 Å. in place of the minimum at 2700 Å. In phenyl orthovanillate, the absorption band having a 3200 Å. maximum has undergone a bathochromic shift, resulting in a 3250 Å. maximum and a 2850 Å. minimum. In addition, one of the twin absorption maxima of the second absorption band has been reduced to a break in the curve, leaving only one maximum at 2530 Å.

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Summary

The ultraviolet absorption spectra of a large number of esters of vanillic acid and the closely related acids, orthovanillic and 5-chlorovanillic, were determined. Spectra for the parent acids and related aldehydes were included.

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